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## Cycling of black carbon in the ocean

Coppola, Alysha I ; Druffel, Ellen R M

**Abstract:** Black carbon (BC) is a byproduct of combustion from wildfires and fossil fuels and is a slow-cycling component of the carbon cycle. Whether BC accumulates and ages on millennial timescales in the world oceans has remained unknown. Here, we quantified dissolved BC (DBC) in marine dissolved organic carbon (DOC) isolated by solid phase extraction (SPE) at several sites in the world ocean. We find that DBC in the Atlantic, Pacific and Arctic oceans ranges from 1.4 to 2.6 M in the surface and is  $1.2 \pm 0.1$  M in the deep Atlantic. The average  $^{14}\text{C}$  age of surface DBC is  $4,800 \pm 620$   $^{14}\text{C}$  yrs, and much older in a deep water sample ( $23,000 \pm 3,000$   $^{14}\text{C}$  yrs). The range of DBC structures and  $^{14}\text{C}$  ages indicates that DBC is not homogeneous in the ocean. We show that there are at least two distinct pools of marine DBC, a younger pool that cycles on centennial timescales and an ancient pool that cycles on  $>10^4$  year timescales.

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## RESEARCH LETTER

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## Key Points:

- DBC in the Atlantic, Pacific, and Arctic oceans ranges from 1.4 to 2.6  $\mu\text{M}$  in DOC isolated by SPE
- The average surface DBC is  $4800 \pm 620$   $^{14}\text{C}$  years and is  $23,000 \pm 3000$   $^{14}\text{C}$  years in the deep
- DBC is not homogeneous indicating that there are at least two distinct pools of marine DBC

## Supporting Information:

- Supporting Information S1

## Correspondence to:

A. I. Coppola,  
alysha.coppola@geo.uzh.ch

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## Cycling of black carbon in the ocean

Alysha I. Coppola<sup>1,2</sup> and Ellen R. M. Druffel<sup>1</sup>
<sup>1</sup>Department of Earth System Science, University of California, Irvine, California, USA, <sup>2</sup>Now at Department of Geography, University of Zurich, Zurich, Switzerland

**Abstract** Black carbon (BC) is a by-product of combustion from wildfires and fossil fuels and is a slow-cycling component of the carbon cycle. Whether BC accumulates and ages on millennial time scales in the world oceans has remained unknown. Here we quantified dissolved BC (DBC) in marine dissolved organic carbon isolated by solid phase extraction at several sites in the world ocean. We find that DBC in the Atlantic, Pacific, and Arctic oceans ranges from 1.4 to 2.6  $\mu\text{M}$  in the surface and is  $1.2 \pm 0.1$   $\mu\text{M}$  in the deep Atlantic. The average  $^{14}\text{C}$  age of surface DBC is  $4800 \pm 620$   $^{14}\text{C}$  years and much older in a deep water sample ( $23,000 \pm 3000$   $^{14}\text{C}$  years). The range of DBC structures and  $^{14}\text{C}$  ages indicates that DBC is not homogeneous in the ocean. We show that there are at least two distinct pools of marine DBC, a younger pool that cycles on centennial time scales and an ancient pool that cycles on  $>10^5$  year time scales.

## 1. Introduction

Biomass burning and fossil fuel combustion release large amounts of greenhouse gases into the atmosphere that are changing Earth's climate [Ciais *et al.*, 2013; Randerson *et al.*, 2012]. In a warmer climate, fire frequency is expected to increase [Ciais *et al.*, 2013]. However, up to 27% of this burned carbon is retained as black carbon (BC) [Kuhlbusch and Crutzen, 1995; Santin *et al.*, 2015]. Black carbon has a range of chemical and physical properties along a continuum from slightly charred biomass to highly aromatic, condensed soot, [Masiello, 2004; Schmidt and Noack, 2000]. However, due to this continuum from char to soot, BC contains multiple carbon pools of various reactivities [Masiello and Louchouart, 2013]. BC can be reactive from century to millennial time scales in soils and the deep ocean [Coppola *et al.*, 2014; Dittmar, 2008; Forbes *et al.*, 2006; Guggenberger *et al.*, 2008; Masiello and Druffel, 1998; Singh *et al.*, 2014a; Ziolkowski and Druffel, 2010]. This study focuses on condensed BC aromatics in the ocean that appear to be refractory [Ziolkowski and Druffel, 2010].

In order to fully understand the carbon cycle, it is critical to know the fate and sources of this slower cycling pool of carbon by characterizing BC cycling through the major carbon reservoirs. Current production estimates exceed the current sink estimates of BC, indicating that there should be more BC than organic carbon in soils [Masiello, 2004; Schmidt, 2004; Stubbins *et al.*, 2012], which is clearly not the case. Mechanisms of removal, e.g., photooxidation and biological degradation, are likely important [Masiello, 2004; Schmidt, 2004; Stubbins *et al.*, 2012]. This large imbalance, combined with the large river transport of BC to the ocean (10% of the terrestrial dissolved organic carbon (DOC) flux) [Jaffe *et al.*, 2013] suggests that BC in the dissolved form (DBC) is stored in an intermediate reservoir, namely, DOC in the ocean [Jaffe *et al.*, 2013; Ziolkowski and Druffel, 2010]. DBC is ubiquitous in freshwater environments, but its fate in the open ocean is unknown.

Here we report the abundance and  $\Delta^{14}\text{C}$  measurements of DBC from the Atlantic, Pacific, and Arctic Oceans (see map in Figure S1 and Table S1). DBC refers to BC within the DOC pool isolated by solid phase extraction (SPE) techniques, which isolates  $43 \pm 5\%$  of the DOC from seawater [Coppola *et al.*, 2015]. DBC was quantified as the polycyclic aromatic carbon as determined from Benzene Polycarboxylic Acid (BPCA) marker compounds produced during high-temperature and pressure acidification [Brodowski *et al.*, 2005; Ziolkowski *et al.*, 2011]. The relative BPCA abundances provide qualitative DBC structural information regarding the aromaticity of the DBC.

## 2. Materials and Methods

## 2.1. Sample Collection

Samples were collected from a site in the northeast Pacific, three sites in the western Arctic, two sites in the North Atlantic, and a site in the southeast Atlantic (Figure S1 and Table S1). Two duplicate northeast Pacific surface (50 m) samples were collected in October 2004 on the Pulse 45 cruise aboard the R/V *New Horizon*.

Western Arctic samples from the Beaufort Sea (~3650–3825 m deep) were collected from adjacent stations (Stn. 40 and 41, 19.4 km apart) taken in October 2012 aboard the R/V *Healy*. A coastal Arctic sample (from 125 to 175 m depths) was also collected. A northeast Atlantic surface (50 m) sample was collected in October 2013 on the A16 cruise aboard the R/V *Brown*. Two deep (1135–2290 m) and one surface (50 m) sample were collected in the North Atlantic from the Sargasso Sea in April 2012 on the A22 cruise aboard the R/V *Atlantis*. The deep Sargasso Sea samples were collected from adjacent stations (Stn. 26 and 27, 83.0 km apart) and were processed separately for DBC concentration and combined for a single DBC  $\Delta^{14}\text{C}$  measurement. A south Atlantic surface (50 m) sample was collected in October 2011 on the A10 cruise aboard the NOAA Ship *Ronald H. Brown*.

All samples were collected in Niskin bottles that had been cleaned at the beginning of each cruise with a dilute detergent solution and 10% hydrochloric acid. Surface samples were filtered using Whatman GF/F filters (0.7  $\mu\text{m}$ ) that had been combusted at 500°C for 2 h. All metal and glassware used in this study was cleaned, acidified in 10% HCl, rinsed with deionized water, and combusted for 2 h at 500°C before use to remove inorganic and organic carbon. DOC samples were collected in 1 L amber glass bottles and DBC samples were collected in 3.785 L, clear glass bottles. All seawater samples were frozen (at  $-20^\circ\text{C}$ , at an angle to avoid breakage) until analysis in the laboratory at University of California Irvine.

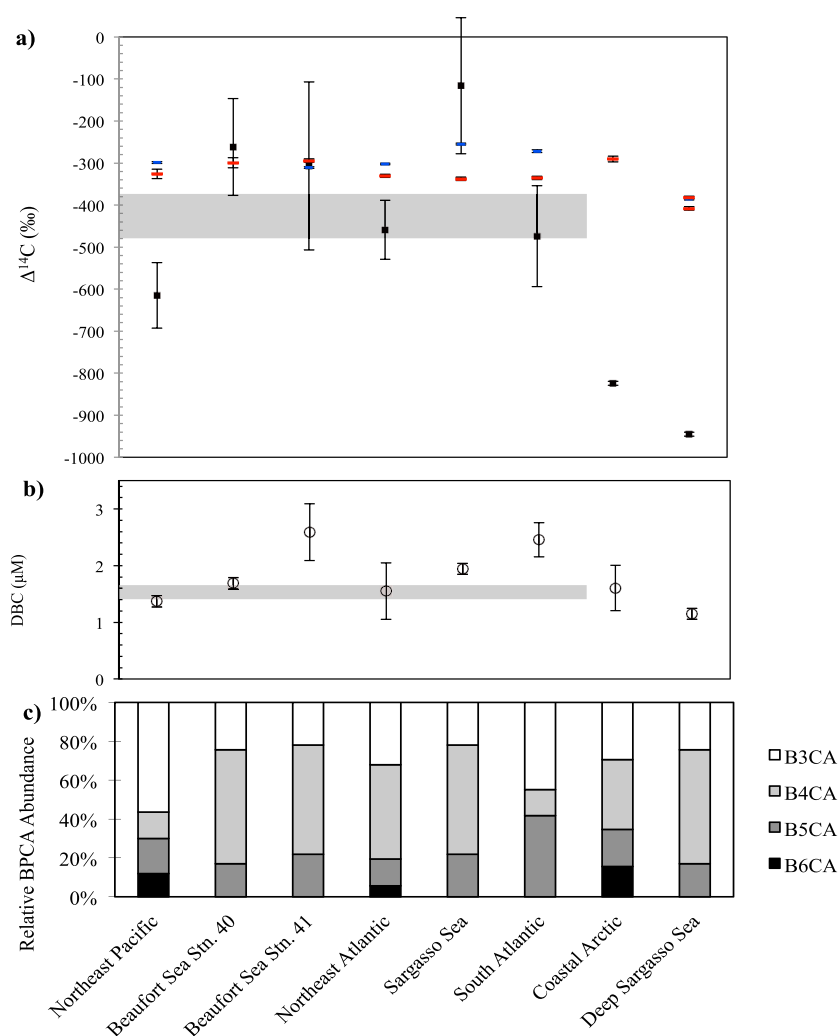
## 2.2. SPE-DOC and Total DOC Concentrations

Seawater samples were measured separately for total DOC (using UV oxidation [Beaupre *et al.*, 2007]) and for SPE-DOC [Coppola *et al.*, 2015]. Briefly, SPE-DOC was extracted from large-volume filtered water samples (10–15 L for surface and 25 L for deep) that had been acidified to pH 2 (using hydrochloric acid, analytical grade) and siphoned through a styrene divinyl benzene copolymer resin (Sigma Aldrich Diaion 13605, HP-20, pore size 200 Å) column at a slow loading rate (two bed volumes per hour,  $240\text{ mL h}^{-1}$ ) [Coppola *et al.*, 2015]. In preparation for DOC elution, two bed volumes (30 mL) of Milli-Q water were passed through the column to remove salts and was discarded. SPE-DOC was eluted with methanol into precombusted glass vials and dried under a stream of ultrahigh purity (UHP) nitrogen gas. SPE-DOC samples were stored at  $-20^\circ\text{C}$  until BPCA analysis.

## 2.3. DBC

DBC was quantified in the SPE-DOC methanol extracts as aromatic marker compounds (benzene polycarboxylic acids, BPCAs) from a high temperature and pressure acid digestion (BPCA method) [Coppola *et al.*, 2013; Ziolkowski *et al.*, 2011]. Briefly, SPE-DOC extracts were dried and lyophilized for 24 h. Concentrated nitric acid was added to the sample in a quartz pressure digestion chamber that was heated to  $170^\circ\text{C}$  for 8 h to produce BPCAs. After digestion, the solution was filtered, lyophilized, and redissolved in methanol. Samples were derivatized using (trimethylsilyl) diazomethane in 2.0 M diethyl ether to convert carboxylic acid groups to methyl esters, and an internal standard was added (diphenic acid). BPCAs were collected on the preparative capillary gas chromatograph (PCGC Hewlett Packard 6890 GC) equipped with an HP 7683B autoinjector, Gerstel cooled injection system (CIS-4) with split/splitless inlet, and a DB-XLB capillary column (30 m  $\times$  0.53 mm ID, 1.5  $\mu\text{m}$  film thickness CP-Sil 8CB Ultimet column). Calibration curves were made using commercially available BPCAs to quantify the BPCAs measured from peak areas obtained from the flame ionization detector chromatographs. The BPCA method requires a conversion factor to convert the BPCAs formed from the nitric acid digestion into an estimate of the original BC mass. A DBC recovery factor of  $23.2 \pm 0.4\%$  was used for the conversion of BPCAs to BC [Ziolkowski and Druffel, 2009; Ziolkowski *et al.*, 2011]. This conversion factor was used because it was determined from oxidizing compounds with known chemical formulas (polycyclic aromatic hydrocarbons) to calibrate the BPCA method for carbon yield. Previously used conversion factors were based on yields from activated charcoal where the chemical formula was unknown [Brodowski *et al.*, 2005; Glaser *et al.*, 1998].

For  $\Delta^{14}\text{C}$  analysis, B3CA through B6CA marker compounds (including nitrated B3CAs and B4CAs) were collected in U-traps ( $-20^\circ\text{C}$ ) in the fraction collector of the PCGC. The B2CA marker compounds were not collected, because they are also derived from aromatic compounds of noncombusted origin (e.g., lignin). Each BPCA may have a unique  $\Delta^{14}\text{C}$  value. However, samples were too small to measure individual BPCA  $\Delta^{14}\text{C}$  values. The BPCAs in the U-trap were transferred using dichloromethane to quartz tubes and dried under UHP nitrogen gas for isotopic analyses.



**Figure 1.** (a)  $\Delta^{14}\text{C}$  values of solid phase extracted dissolved organic carbon (SPE-DOC, red dashes), total dissolved organic carbon (DOC, blue dashes), and dissolved black carbon (DBC, black squares) samples. All samples are from the surface, except the deep Sargasso Sea sample. The average DBC  $\Delta^{14}\text{C}$  value for the surface ocean (excluding the coastal Arctic) is  $-450 \pm 42$ ‰ and is displayed as the grey box. (b) DBC concentration values. The average DBC concentration for the surface samples is  $1.6 \pm 0.1$   $\mu\text{M}$  and is displayed as the grey box. (c) Relative BPCA abundances in each DBC sample.

## 2.4. Radiocarbon Analysis

Samples were sealed in quartz tubes under vacuum with cupric oxide and silver wire and combusted to  $\text{CO}_2$  at  $850^\circ\text{C}$  for 2 h. The  $\text{CO}_2$  was cryogenically purified, quantified manometrically, and reduced to graphite using a hydrogen reduction method for small samples [Santos *et al.*, 2007]. Radiocarbon measurements were made at the University of California Irvine Keck Carbon Cycle Accelerator Mass Spectrometry Laboratory and are reported as  $\Delta^{14}\text{C}$  (and conventional  $^{14}\text{C}$  age) for geochemical samples without known age [Stuiver and Polach, 1977]. Stable carbon isotopes ( $\delta^{13}\text{C}$ ) were measured on equilibrated splits of  $\text{CO}_2$  from a subset of the DOC and SPE-DOC samples using a Gas Bench II and Thermo Electron Delta Plus mass spectrometer with an uncertainty of  $\pm 0.2$ ‰. Stable carbon isotopes were not measured on BPCAs due to the small sample sizes.

## 3. Results

We obtained surface DBC  $\Delta^{14}\text{C}$  values that ranged from  $-116 \pm 162$  (Sargasso Sea) to  $-824 \pm 5$ ‰ (coastal Arctic) (Figure 1a and Table S2). The average surface DBC  $\Delta^{14}\text{C}$  value for open ocean samples was  $-450 \pm 42$ ‰ ( $4800 \pm 620$   $^{14}\text{C}$  years,  $n = 6$ ). The coastal Arctic sample was excluded in this average because it was

not an open ocean sample. The deep Sargasso Sea sample had the lowest DBC  $\Delta^{14}\text{C}$  value ( $-945 \pm 6\text{‰}$ ;  $23,000 \pm 3000$   $^{14}\text{C}$  years) obtained in this study.

In contrast, the surface SPE-DOC  $\Delta^{14}\text{C}$  measurements (Figure 1a) ranged from  $-290 \pm 3$  in the coastal Arctic to  $-338 \pm 4\text{‰}$  in the Sargasso Sea. The Beaufort Sea SPE-DOC  $\Delta^{14}\text{C}$  values from adjacent stations were identical ( $-294 \pm 4$  and  $-299 \pm 4\text{‰}$ ). The northeast Atlantic, Sargasso Sea, and south Atlantic SPE-DOC  $\Delta^{14}\text{C}$  values were also identical ( $-330 \pm 4$ ,  $-338 \pm 4$ , and  $-335 \pm 7\text{‰}$ , respectively). Two deep Sargasso Sea samples at Stn. 26 and Stn. 27 had significantly different values ( $-382 \pm 4$  and  $-408 \pm 4\text{‰}$ , respectively).

The relatively narrow range of SPE-DOC  $\Delta^{14}\text{C}$  values is comparable to the range of total DOC  $\Delta^{14}\text{C}$  values obtained for these samples (Table S2). Surface total DOC  $\Delta^{14}\text{C}$  measurements (Table S2 and Figure 1a) ranged from  $-255 \pm 4\text{‰}$  in the Sargasso Sea to  $-311 \pm 4\text{‰}$  in the Beaufort Sea, respectively. The total DOC  $\Delta^{14}\text{C}$  values are significantly higher than their requisite SPE-DOC  $\Delta^{14}\text{C}$  values for four samples, significantly lower for one sample (Beaufort Sea, Stn. 41) and the same for one sample (Sargasso Sea, Stn. 26).

The concentrations of DOC in the surface samples ranged from 53.8 to 71.8  $\mu\text{M}$  (Table S2). The DOC concentration in the deep Sargasso Sea was 42.1  $\mu\text{M}$ . These values are within error of DOC concentrations reported by Hansell *et al.* [2009]. The recovery for marine SPE-DOC was  $43 \pm 2\%$ , which is within error of the recovery reported by Dittmar [2008] using a similar resin. Surface SPE-DOC concentrations ranged from 25.9 to 32.0  $\mu\text{M}$  (Table S2). The deep Sargasso Sea SPE-DOC concentrations at adjacent stations were 22.1 and 23.5  $\mu\text{M}$ .

DBC in the surface samples ranged from 1.4 to 2.6  $\mu\text{M}$ . The lowest surface DBC concentration was in the northeast Pacific, while the highest were in the Beaufort Sea and south Atlantic ( $2.6 \pm 0.9$  and  $2.5 \pm 0.4$   $\mu\text{M}$ , respectively). The average surface DBC concentration was  $1.6 \pm 0.1$   $\mu\text{M}$  ( $n = 6$ ). The average DBC concentration of two deep Sargasso Sea samples was  $1.2 \pm 0.1$   $\mu\text{M}$ .

For most DBC samples, B3CAs and B4CAs were more abundant than the B5CAs and B6CAs (Figure 1c). B5CA and B6CA marker compounds (which are indicative of highly aromatic, condensed BC), constituted 15–30% of the BPCAs quantified. Higher relative abundances of B3CAs were observed in the northeast Pacific and south Atlantic samples.

#### 4. Discussion

It was hypothesized that DBC was the ancient component responsible for the low  $\Delta^{14}\text{C}$  values of total DOC [Ziolkowski and Druffel, 2010; Masiello and Druffel, 1998]. We find that the concentration and  $\Delta^{14}\text{C}$  value of DBC in the deep Sargasso Sea (1.2  $\mu\text{M}$  and  $-945\text{‰}$ ) does not explain the low  $\Delta^{14}\text{C}$  value of SPE-DOC (20  $\mu\text{M}$  and  $-395\text{‰}$ ). If DBC was not present in SPE-DOC, the  $\Delta^{14}\text{C}$  of SPE-DOC in the deep Sargasso Sea sample would be  $-360\text{‰}$ , which is only 35 $\text{‰}$  higher than its present value ( $-395\text{‰} = (1.2 \mu\text{M}/20 \mu\text{M}) * (-945\text{‰}) + (18.8 \mu\text{M}/20 \mu\text{M}) * x$ ). Clearly, other  $^{14}\text{C}$ -depleted components besides DBC must be present to account for the great  $^{14}\text{C}$  age of DOC.

Importantly, our data reveal that there is a minimum of two pools of DBC in the ocean, each with its own  $^{14}\text{C}$  age. It is not possible to model DBC as a homogenous pool with a single  $\Delta^{14}\text{C}$  value (supporting information, Text S1, Figure S3, and Figure S4). Using a simple mass balance, the surface ocean average value ( $-450\text{‰}$ ) can be obtained from a mixture of postbomb DBC ( $+1035 \pm 521\text{‰} = x$ ) and the deep Sargasso Sea DBC ( $-945 \pm 6\text{‰}$ ) ( $-450\text{‰} = (0.4 \mu\text{M}/1.6 \mu\text{M}) * x + (1.2 \mu\text{M}/1.6 \mu\text{M}) * (-945\text{‰})$ ).

DBC entering the ocean from rivers and aerosols have different physical properties and structures than those in the ocean, which likely affect their residence times [Ding *et al.*, 2015; Safai *et al.*, 2014; Santin *et al.*, 2015]. For example, land-derived BC may be more important in some regions (e.g., Arctic) than in others (e.g., South Pacific) [Stubbins *et al.*, 2015], and we hypothesize that it may contain more bomb  $^{14}\text{C}$ . The second pool is an ancient, more stable DBC pool ( $>20,000$   $^{14}\text{C}$  years) that likely predominates in the deep ocean [Ziolkowski and Druffel, 2010].

Simple mixing of two isotopically different components of DOC was reported earlier [Druffel *et al.*, 1992; Williams and Druffel, 1987]. Specifically, mixing of a labile DOC pool at the surface (from primary production), with aged DOC from deep water explains the total DOC concentrations and  $\Delta^{14}\text{C}$  values in the surface waters of the Sargasso Sea, Mid-Atlantic Bight, north central, and northeastern Pacific [Bauer *et al.*, 1998; Druffel *et al.*, 1992;

Williams and Druffel, 1987] (supporting information Text S1). Two-component mixing is also observed for BC in soils, where there are two BC pools with distinct chemical compositions and residence times [Bird *et al.*, 2015; Knicker *et al.*, 2013; Singh *et al.*, 2012, 2014b]. Because oceanic DBC is coupled to riverine DOC export globally [Ding *et al.*, 2015; Jaffe *et al.*, 2013; Wagner *et al.*, 2015], DBC pools with different structures and  $^{14}\text{C}$  ages may be preserved in the ocean and may explain the two DBC pools that we observe.

If we assume that the global ocean has similar DBC and SPE-DOC concentrations as those found in our study, the mass of DBC in the global SPE-DOC pool would be  $14 \pm 2 \text{ Gt C}$  ( $662 \text{ Gt C} \times 0.43 \times 0.05 = 14 \text{ Gt C}$ ). This value is similar to a previous estimate (12 Gt) [Dittmar and Paeng, 2009]. This technique, which encompasses SPE extraction through oxidation, extraction, and quantification of the BPCA derivatives from DBC, provides a conservative estimate of the total DBC mass.

Our estimate of DBC mass does not include 57% of the total DOC pool, given that 43% of the DOC was sorbed onto the SPE resin and quantified. The distribution of DBC in total DOC has not been measured. If DBC is equally distributed in the non-SPE-DOC pool, then our estimate of the mass of DBC in the global DOC pool is  $32 \pm 4 \text{ Gt DBC}$  ( $662 \text{ Gt DOC} \times 0.05$ ). This value would require modification if BC is unequally distributed in DOC as an Arctic river study and a natural organic matter Suwannee River standard assessment suggest [Wagner and Jaffe, 2015; Coppola *et al.*, 2015]. DBC in SPE-DOC isolates are more aromatically condensed and may have higher  $\Delta^{14}\text{C}$  values than those of DBC from the total DBC pool [Coppola *et al.*, 2015]. It is highly likely that there is discreet cycling of DBC within these DOC fractions isolated by different techniques. Nonetheless, a larger sample set and comparisons of BC isolated in various size fractions and using different SPE techniques are needed to quantify the relationship of DBC in DOC.

Our study presents the first assessment of SPE-extracted DBC  $^{14}\text{C}$  ages in ocean water. Each year, rivers transport  $0.0265 \pm 0.0018 \text{ Gt DBC}$  to the oceans [Jaffe *et al.*, 2013]. Atmospheric deposition is a smaller source of BC to the ocean, ranging from 0.002 to 0.006 Gt DBC per year in the Northern Hemisphere [Jurado *et al.*, 2008]. The input by rivers is sufficient to sustain the turnover of the entire DBC pool in 500  $^{14}\text{C}$  years, yet  $^{14}\text{C}$  ages are 40 times higher for DBC in the deep sea. We estimate that the amount of DBC in the SPE-DOC is low,  $14 \pm 2 \text{ Gt C}$ , with old  $^{14}\text{C}$  ages in the surface ( $4800 \pm 620 \text{ }^{14}\text{C}$  years) and deep ( $23,000 \pm 3000 \text{ }^{14}\text{C}$  years) ocean. This suggests that despite its polyaromatic structure, most BC delivered via rivers is not accumulating in the ocean. Therefore, loss processes, such as UV oxidation and microbial degradation, may be important for altering and removing DBC [Stubbins *et al.*, 2012]. Additionally, with recent increases of burning of fossil fuels and biomass, DBC export from river systems will continue to rise [Randerson *et al.*, 2012]. Riverine and atmospheric DBC  $\Delta^{14}\text{C}$ , structure, and concentration measurements will help to understand the input and fate of DBC into the DOC pool from watersheds to the deep ocean.

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